

# Polymer electrolyte membrane water electrolysis: status of technologies and potential applications in combination with renewable power sources

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**Abstract** Technological improvements in polymer electrolyte membrane water electrolyzers (PEMWEs) are promoted by their exciting possibilities to operate with renewable power sources. In this paper, a synopsis of the research efforts concerning with the development of electrocatalysts, polymer electrolytes and stack hardware components is presented. The most challenging problem for the development of PEMWEs is the enhancement of oxygen evolution reaction rate. At present, there are no practical alternatives to noble metal-based oxide catalysts such as  $\text{IrO}_2$  and  $\text{RuO}_2$ . As well as carbon supported Pt nanoparticles are the benchmark cathode catalysts for hydrogen evolution. High noble metal loading on the electrodes and the use of perfluorosulfonic membranes significantly contribute to the cost of these devices. Critical areas include the design of appropriate mixed electrocatalysts and their dispersion on low cost Ti-oxide like supports to increase catalyst utilization. Moreover, the development of alternative membranes with enhanced mechanical properties for high pressure applications, proper conductivity and reduced gas cross-over is strongly required. This latter aspect is also addressed by the development of proper recombination catalysts. The development of anodic mixed non-noble transition metal oxides with spinel or perovskite structure and proper resistance to chemical degradation in the acidic environment and electrochemical corrosion is also an active area of research. Similarly, efforts are also being addressed to Pd and Ru based cathode formulations with cheaper characteristics than Pt. Whereas, concerning

with stack hardware, cost reduction may be addressed by replacing Ti-based diffusion media and bipolar plates with appropriate and cost-effective stainless steel materials with enhanced resilience to chemical and electrochemical corrosion. Regarding the combination with renewable power sources, PEM electrolyzers can find suitable applications for peak shaving in integrated systems grid connected or in grid independent operating conditions where hydrogen generated through electrolysis is stored and then via fuel cell converted back to electricity when needed or used to refill fuel cell-based cars. Hydrogen is the most promising clean energy carrier to accomplish the sustainable production of energy and a synergy among hydrogen, electricity and renewable energy sources is highly desired.

**Keywords** Water electrolysis · Polymer electrolyte membrane · Oxygen evolution · Hydrogen evolution · Electrocatalysts · Renewable energy sources

## 1 Introduction

Hydrogen is a promising energy carrier that can be produced by various technologies such as reforming of hydrocarbons, gasification of biomass, electrolysis of water using nuclear, fossil or renewable energy sources, photocatalytic water splitting and thermolysis. Among these pathways, electrolysis of water using renewable energy sources (RES) is an essential contributor, due to the relatively high efficiency ( $\sim 70\%$ ) and the production of high purity hydrogen [1–4]. Overcapacities in electricity production from renewable power sources can be suitably addressed by converting the surplus of electrical energy into hydrogen. Renewable energy sources/electrolyser pilot plants have shown that they can be matched directly with high coupling efficiency [1].

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Several processes and devices are currently developed for water electrolysis such as alkaline systems, solid oxide electrolyte and proton exchange membrane (PEM)-based electrolyzers. PEM water electrolysis is considered the most promising method to produce hydrogen with a high degree of purity from renewable energy resources such as wind, photovoltaic and hydropower [1]. The process is characterized by high efficiencies and suitable current density even at moderate temperatures. PEM electrolysis systems have a number of advantages in comparison to the traditional alkaline electrolyzers, such as ecological cleanliness, considerably smaller mass-volume characteristics, no corrosive electrolyte is involved, low maintenance and, essentially, a high degree of gas purity [2]. There is also the opportunity to obtain compressed gases directly from the electrolyzer at an increased level of safety [1]. The main disadvantage of PEM electrolysis is the high cost, which is mainly due to the use of noble metal catalysts, perfluorinated membranes and titanium current collectors [3]. Thus, in order to be competitive within the field of decentralised hydrogen production and especially for small scale applications such as residential homes under operation with renewable power sources, the PEM electrolyzer must be reasonably cheap; moreover, it should be compact, characterised by high durability and capable of producing hydrogen at high efficiency and at suitable pressure.

At present, challenging problems to the development of such systems remain. Electrochemical water splitting is associated with substantial energy loss. The oxygen evolution electrode (anode) is the main source of overpotential in this system. But, at high current density, also the contribution of the polymer membrane electrolyte resistance is quite significant. In addition, mechanical, chemical and electrochemical stability play an important role. It is therefore important to develop optimal oxygen-evolving electro-catalysts, and highly conductive and mechanically robust membranes in order to minimize energy loss and enhance system durability. Before this technology can reach a full scale production, problems related to high cost and short term stability must be solved.

The aim of the present work is to review the status of technologies for polymer electrolyte membrane water electrolyzers and their potential applications in combination with renewable power sources. Particular efforts are addressed to the analysis of the research activities concerning with active components, materials activity and stability. Presently, the active materials contribute to about 70 % of stack costs. Thus, the focus of next research activities will necessarily concern with low-cost electrocatalyst, low-noble metal loading electrodes and cost-effective membranes. At the same time further improvements are necessary with regard to backing layers and stack hardware. All these research efforts

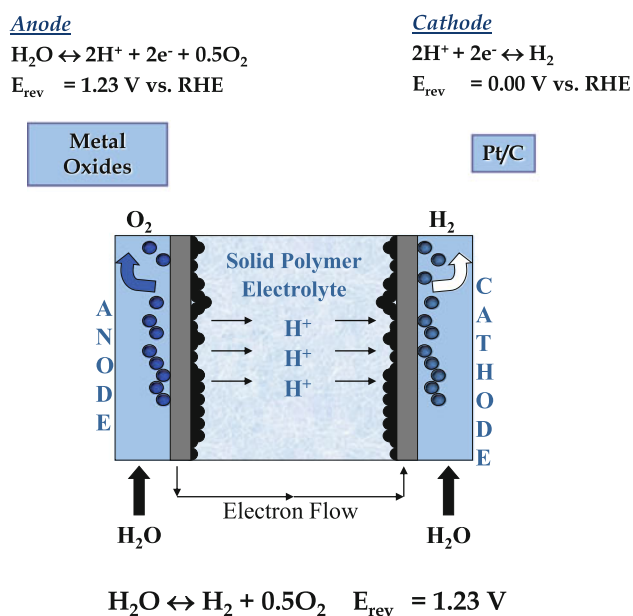
should be addressed to reduce stack and system costs and to improve efficiency, performance and durability. The main perspective regard a suitable integration with renewable power sources. Advanced and cost-effective PEM electrolyzer may contribute to the road-map addressing the achievement of a wide scale decentralised hydrogen production infrastructure.

## 2 Water electrolysis and related technologies

Electrolysis of water is the dissociation of water molecules into hydrogen and oxygen gases. For this process, in the presence of liquid water at 298 K and 1 bar,  $\Delta G^\circ$  is 237 kJ mol<sup>-1</sup> (corresponding to  $\sim 1.23$  V),  $\Delta S^\circ$  is 163 J mol<sup>-1</sup> K<sup>-1</sup> ( $T\Delta S^\circ \sim 0.25$  V) whereas  $\Delta H^\circ$  is 286 kJ mol<sup>-1</sup>. The thermo-neutral potential at which this reaction occurs in absence of external heat supply is  $E_{th,\Delta H} = 1.48$  V (upper heating value 3.54 kWh Nm<sup>-3</sup> H<sub>2</sub>) [2]. If steam is fed to the device, the reaction enthalpy is reduced by  $\sim 40$  kJ mol<sup>-1</sup> corresponding to the vaporisation enthalpy. Water electrolysis is traditionally carried out in alkaline media with several commercial electrolyzers available on the market. Water electrolyzers using a solid polymer electrolyte are less common and generally use expensive materials such as noble metal electrocatalysts and Nafion membranes [1]. However, PEMWEs have recently received considerable attention because they offer the possibility of achieving higher energy efficiencies. The production capacity of the present commercial PEM electrolyzers (up to a few tens of Nm<sup>3</sup> H<sub>2</sub> h<sup>-1</sup>) is generally smaller than that of alkaline technology (hundreds of Nm<sup>3</sup> H<sub>2</sub> h<sup>-1</sup>) [1]. PEMWEs are especially envisaged for small utilities. However, a significant reduction of the cost of active components may allow a proper scale-up of these systems to the same level of alkaline electrolyzers at reasonable costs that, combined with the reduced maintenance levels, can make them very competitive.

The principle of operation of a PEM water electrolyzer is reported in Fig. 1. In the PEM water electrolyzer (PEMWE), when a voltage larger than the thermo-neutral potential for water splitting ( $E_{th,\Delta H} = 1.48$  V at 80 °C) is applied across the electrochemical cell reactions occur at both electrodes. The reaction rate for water splitting is determined by the applied potential, temperature, anode and cathode electrocatalyst characteristics, and membrane resistance.

In alkaline electrolyzers, a liquid electrolyte, typically a 30 % KOH is used; they operate at relatively low current densities ( $<0.4$  A cm<sup>-2</sup>) and conversion efficiencies approach 60 % versus LHV. Without auxiliary purification equipment, gas purities are typically 99.8 and 99.2 % for H<sub>2</sub> and O<sub>2</sub>, respectively. Since high currents are necessary



**Fig. 1** Principle of operation of a PEM water electrolysis cell

to reduce investment costs, this characteristic, the modest gas purity and the presence of a caustic electrolyte are the main drawbacks [1]. The key factors favouring the alkaline electrolyser are that it obviates the need for a high content of expensive noble-based catalysts, in fact, this system uses nickel, coated with a film of platinum as the cathode catalyst and nickel or copper coated with metal oxides (Mn, Ru or W) as the anode catalyst as well as the cheap liquid electrolyte. Thus, to make PEMWEs competitive versus alkaline electrolyzers, it is necessary to bring about cost reduction of the active components.

The present PEM electrolyzers require use of noble metals such as platinum as cathode catalyst and iridium or ruthenium oxide as anode catalyst at several  $\text{mg cm}^{-2}$ . PEMWEs can reach high current densities ( $1\text{--}2 \text{ A cm}^{-2}$  at  $1.8\text{--}2.1 \text{ V}$ , respectively, at  $90^\circ\text{C}$  [2]) and achieve efficiencies at  $1 \text{ A cm}^{-2}$  of 70 % versus LHV or 80 % versus HHV [2].

The inherent advantages of PEM technology over alkaline are clearly established: greater safety and reliability are expected since no caustic electrolyte is circulated in the cell stack; possibility to operate at high differential pressures, resulting in the production of pressurised gases, thus reducing the auxiliary gas compression; the possibility of operating cells at high current densities is afforded. However, at these conditions, the heat generated exceeds largely the heat required to maintain the temperature and cooling is needed. Moreover corrosion aspects are exacerbated by the high electrochemical potential ( $>2 \text{ V}$ ). Lower operating voltages ( $1.6 \text{ V}$ ) are preferable if

efficiency, thermal management and durability are more important than the capital cost of the electrolyser or cheaper active components are developed.

Presently, there are only a few industrial PEMWEs manufacturers (GE, Giner, NorskHydro, Proton, ITM). The Proton Energy Systems produces the HOGEN<sup>®</sup> 40 for industrial applications and the HOGEN<sup>®</sup> RE for use in conjunction with renewable power sources [1]. The latter has a hydrogen production capacity of  $0.5\text{--}1 \text{ Nm}^3 \text{ h}^{-1}$  with a corresponding power consumption for the system of  $6.6 \text{ kWh Nm}^{-3} \text{ H}_2$ . The power consumption is about  $5.6 \text{ kWh Nm}^{-3} \text{ H}_2$  for the Giner PEM stack. The contribution of the auxiliaries at the maximum capacity is less than 10 % of the total electric power consumption. Similar performances are reported by the other PEMWE manufacturers.

According to the DOE [4], the target efficiency at 2017 is fixed at 74 % versus LHV  $\text{H}_2$  that is not significantly larger than the best present state of the art (70 % vs. LHV  $\text{H}_2$ ). Thus, it appears clear that most of the efforts should be addressed to the decrease of the capital costs.

### 3 Materials challenges in PEM water electrolysis

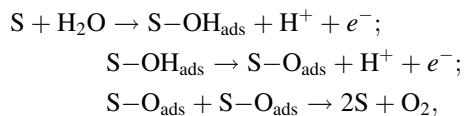
The development of PEMWEs for operation with renewable sources requires appropriate materials research to develop the particular and demanding set of properties required by the device i.e. suitable mechanical resistance for the membranes under high pressure operation, absence of gas cross-over, high catalytic activity, suitable corrosion resistance, high performance and durability.

Regarding electrocatalysts, platinum is typically used at the cathode for the hydrogen evolution reaction (HER) and unsupported iridium or ruthenium oxides are used at the anode for the oxygen evolution reaction (OER) [3, 5–10]. Whereas perfluorosulphonic acid membrane are the benchmark electrolytes for PEMWEs.

#### 3.1 Anode electrocatalysts

The rate determining step in PEMWEs is associated with the oxygen evolution process occurring at the anode [3]. Several oxygen evolution reaction mechanisms have been proposed, however few actually take into consideration the nature of the electrode surface, which is critical for understanding the real reaction mechanism. Metal oxides are most frequently used as anodes in acidic media but most transition metal oxides such as Ni, Co and Mn, if not properly stabilised, undergo corrosion under these conditions. The cations of these metals are known to poison the membrane by exchanging the sulphonic acid groups, thereby reducing the conductivity of the membrane. Platinum group metal (PGM) oxides such as  $\text{RuO}_2$  and  $\text{IrO}_2$  and

some metal oxide supports such as  $\text{TiO}_x$  and  $\text{SnO}_x$ , have been found to be more stable during the OER [11–13]. Oxygen evolution occurs above the thermoneutral potential of 1.48 V. This value is above of the standard potential of almost all solid materials, explaining why only a few materials are stable under the OER. In acid medium, the reaction mechanism of  $\text{O}_2$  evolution is exemplified below:



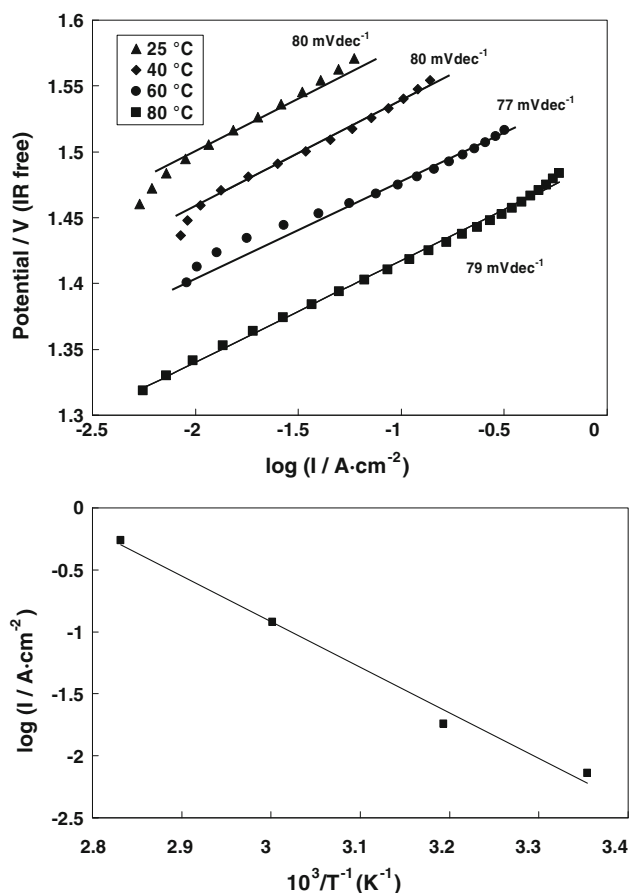
where S represents active sites on the catalyst surface, and  $\text{S}-\text{OH}_{\text{ads}}$ ,  $\text{S}-\text{O}_{\text{ads}}$  are adsorption intermediates [14, 15]. Which step is the rds depends on the strength of the adsorption of the intermediates, which is in turn governed by the surface characteristics of the oxide layer. Since there are no non-precious metal electrocatalysts with satisfactory activities yet developed, it becomes vital, as a first approach, to reduce production costs by improving the specific performance and durability of noble metal electrocatalysts. Various studies have identified the guidelines for the choice of oxide electrocatalysts for OER in relation to the redox potentials of the metal/metal oxide couple, indicating that the reaction mechanism is governed by the surface electrochemistry [15].

The water electrolysis process is thermally and potential activated as can be observed in Fig. 2. However, above 80 °C, side effects such as membrane dehydration and ionomer dry-out cause a modification of this behaviour unless special electrolytes and high pressure operating conditions are used.

As above mentioned, due to the electrochemical stability requirements, the most common electrocatalysts for the oxygen evolution reaction (OER) beside being quite expensive noble metal oxides, e.g.  $\text{IrO}_2$ ,  $\text{RuO}_2$ , are also currently used in the unsupported form at several  $\text{mg cm}^{-2}$  [3]. Accordingly, they are characterised by low surface area and poor catalyst utilization. Moreover, the unsupported catalysts are more susceptible to sintering and agglomeration than supported catalysts.

At present, it is essential to reduce the amount of noble metal electrocatalyst loaded in the electrodes by about one order of magnitude. This may be achieved by supporting nanosized electrocatalyst particles on a high surface area conducting support. The support provides a physical surface for the dispersion of small particles of the active phase, which is necessary for achieving high surface area as required to increase the number of catalytic sites involved in the reactions.

In fact, supported electrocatalysts can significantly enhance the dispersion of the active phase, provide high surface area and a large number of catalytic sites for oxygen evolution. A synergistic role of the support in terms of performance and stability can be played through



**Fig. 2** Electrochemical and temperature activation effects for a PEM electrolysis process [19]. The Tafel slope is the sum of anode and cathode contribution

catalyst-support interaction. Despite these positive aspects, several requisites for the support including chemical and electrochemical stability, high conductivity, high surface area and capability of enhancing dispersion of active phase has limited the development of supported electro-catalysts for oxygen evolution.

The anode catalyst needs to be highly active and stable in an operating potential range up to 2 V versus RHE. Whereas the cathode operates just below 0 V RHE; the corrosion problems are strongly mitigated by the low operating potential and the designed electrocatalyst, i.e. Pt, is commonly supported on a high surface area carbon black. The development of stable supports is thus strongly required for the oxygen evolution catalysts to enhance dispersion, improve electrochemical stability and reduce noble metal content [13].

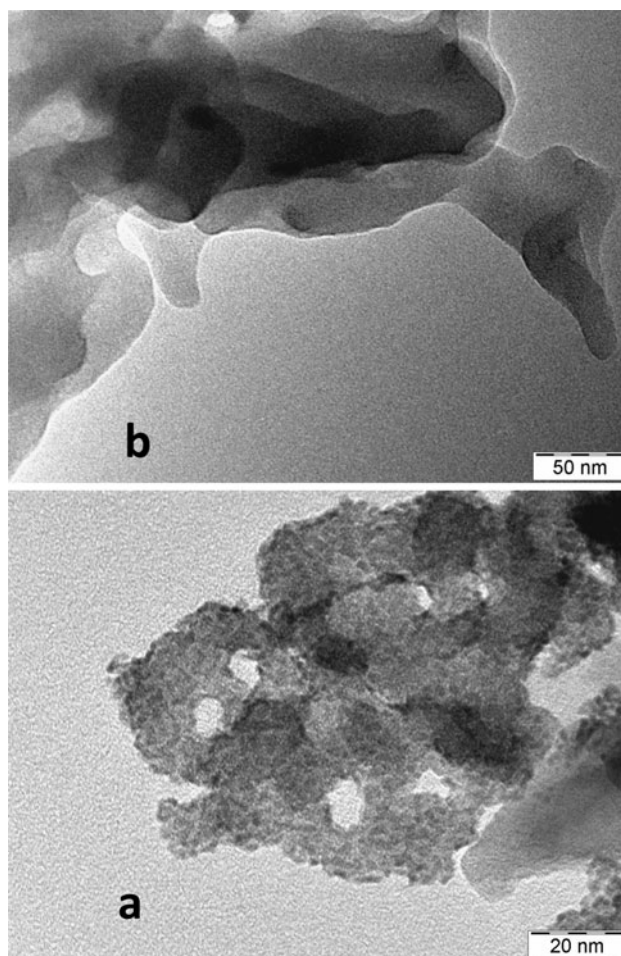
An interesting approach to reduce costs and enhance the electrocatalysis of  $\text{O}_2$  evolution is by forming solid solution of Ir with less expensive transition metal oxides as well as with Ru to form stable and active mixed oxides. In several cases, alloyed and non-alloyed Ir-M and IrRuM oxide



catalysts (with M non noble metal such as Ta, Mo) present suitable OER rate. Although a comprehensive understanding has not been reached, such synergistic effects in enhancing electrocatalytic activity have been ascribed to several factors (interatomic spacing, preferred orientation, electronic interactions) which play, under PEM electrolyser conditions, a favourable role in enhancing the OER rate. On the other hand, the occurrence of electro-positive elements on the surface may cause the onset of corrosion phenomena in acidic environments especially at the high operating potentials of the PEM electrolyser. In this regard, core-shell structures containing the base-metal in the bulk of oxide nanoparticles and noble-metal on the outermost layers are highly appealing.

In the literature, supporting materials for electrocatalysts like boron carbide, tantalum boride and titanium carbide have been investigated. Conductive suboxides of titanium, such as Ebonex<sup>®</sup>, have been studied for various electrochemical applications [16, 17]. Unfortunately, most of these oxide and sub-oxides supports are characterised by low surface area which makes difficult an effective dispersion of the active catalytic phase. This is the main reason why such supports have not yet found suitable application in PEM electrolysis. A suitable process for preparing Ti-suboxides and/or doped oxides (TiTaOx, TiNbOx, SnSbOx) with high surface area is mandatory. The surface area of commercial Ti-suboxides (Ebonex) is  $1.6 \text{ m}^2 \text{ g}^{-1}$  [13], whereas it must be at least two orders of magnitude larger to allow for a good dispersion of the active phase. A meso-porous morphology is also needed. Novel chemical routes have shown that it is possible to prepare such sub-oxides and doped oxides with significantly larger surface area and optimal electronic conductivity [13]. A specific optimization may further enhance the support properties for application in oxygen electrodes. However, recent attempts have been made to obtain suitable dispersion of IrO<sub>2</sub> on Ti-suboxides characterised by a Magneli phase (Fig. 3) with encouraging results [13].

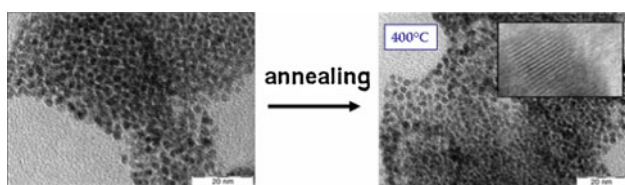
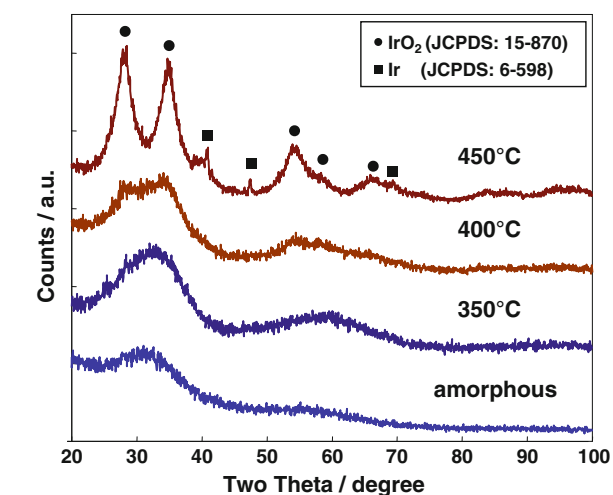
As above discussed, regarding oxygen evolution, most of the non-noble metal oxides are subject to corrosion in acidic environment and are thus not suitable as catalysts for the oxygen evolution under the specific reaction conditions. IrO<sub>2</sub> is the most used anode catalyst for OER; it exhibits high corrosion resistance and shows only slightly inferior activity compared to RuO<sub>2</sub> [3]. Although RuO<sub>2</sub> is more performing in the low overpotential range, its poor stability [8] has precluded practical application; the use of binary IrO<sub>2</sub>–RuO<sub>2</sub> solid solutions can mitigate the instability of RuO<sub>2</sub> but not yet at satisfactory levels [9, 18]. High dispersion and number of active catalytic sites on the surface of the IrO<sub>2</sub> supported on the sub-oxides or doped oxides may considerably enhance catalytic activity. Accordingly, most preparation methods for IrO<sub>2</sub> aim at obtaining



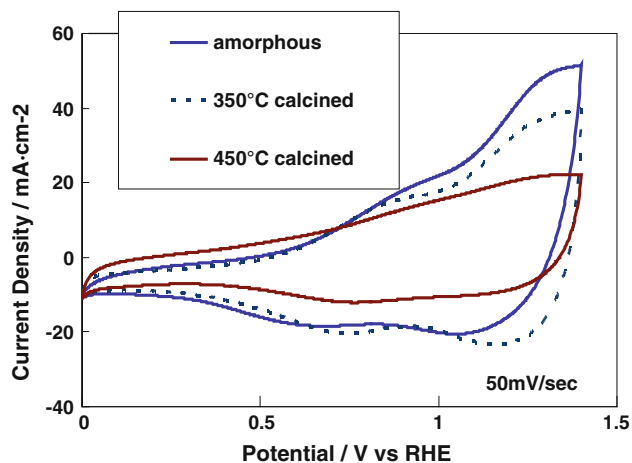
**Fig. 3** Ti-suboxide (Magneli phase) support with (a) and without (b) a dispersed IrO<sub>2</sub> phase. Reprinted from Ref. [13] with permission from Elsevier

nanosized primary particles. Moreover, the oxygen evolution process (rate determining step) being a structure sensitive reaction, it is important to tailor the structural properties of IrO<sub>2</sub> that determine the turnover frequency of the catalytic process. A crystalline tetragonal structure for IrO<sub>2</sub> is preferred in terms of specific activity [6].

A drawback of several IrO<sub>2</sub> preparation methods is of the presence of chlorine residues of chloride-based precursors. Chlorine species are retained on the surface even after high temperature treatments (e.g. 400 °C) poisoning the catalyst and causing loss of catalytic activity. Furthermore, chlorine species make difficult an appropriate control of the particle size during the synthesis of Ir-oxide. It is possible to address the synthesis of nanosized IrO<sub>2</sub> catalysts by using alternative routes with respect to the conventional methods. New synthesis procedures leading to a crystallite size of 2–3 nm with reduced degree of sintering are necessary. Recently, alternative sulphite-based precursors have been investigated for preparation of nanosized

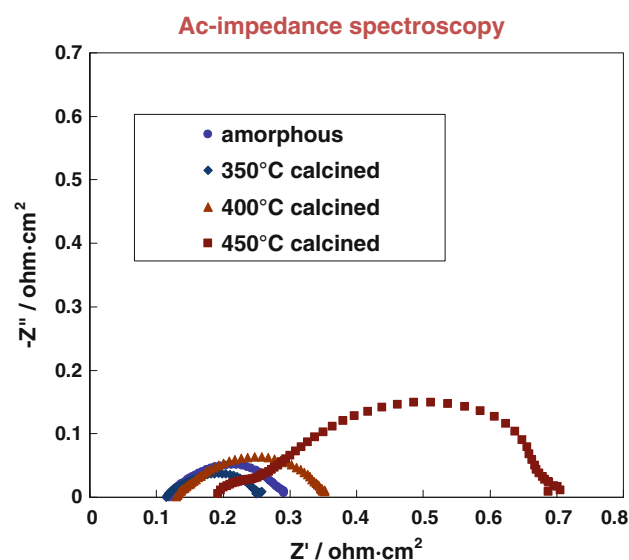
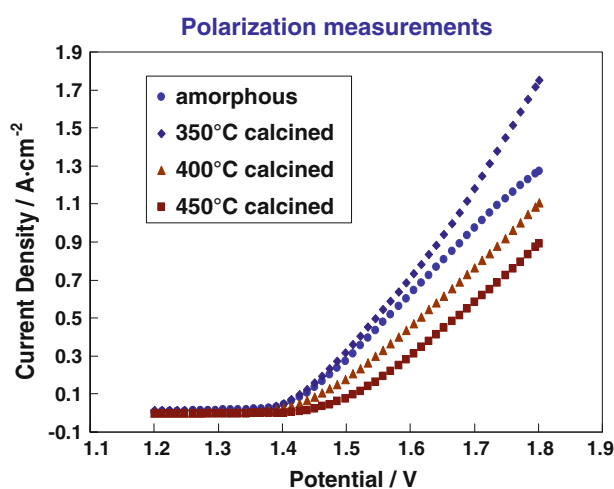


**Fig. 4** Evolution of structural and morphology characteristics of a benchmark unsupported IrO<sub>2</sub> anode catalyst as function of the annealing temperature [6]



**Fig. 5** Electrochemical active surface area changes for an unsupported IrO<sub>2</sub> anode catalyst as function of the annealing temperature [6]

IrO<sub>2</sub> [19]. Such compounds do not show the chlorine-based precursor drawbacks in low temperature electrochemistry. As above discussed the oxygen evolution rate depends strongly on the electrocatalyst chemistry, structure, and morphology. For IrO<sub>2</sub> catalysts, these characteristics can be modulated by varying the annealing temperature (Fig. 4) resulting in different electrochemically active surface area (Fig. 5) and performance characteristics (Fig. 6).

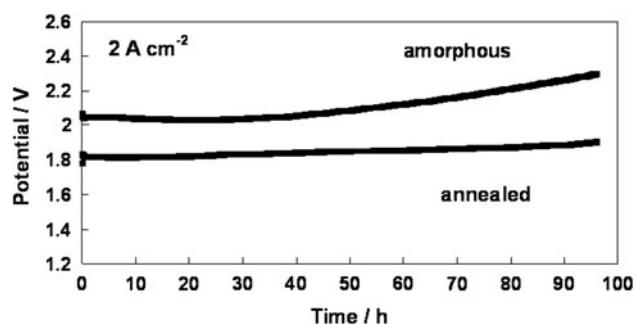


**Fig. 6** Polarization measurements and ac-impedance spectra (1.5 V) for a PEM water electrolysis cell based on various unsupported IrO<sub>2</sub> anode and Pt/C cathode electrocatalysts [6]

The performance achieved in a PEM electrolyser single cell for nanosized IrO<sub>2</sub> electrocatalysts in combination with a Pt/C cathode is shown in Fig. 6. Polarization curves and ac-impedance spectra clearly show that the best performance is achieved at intermediate annealing temperatures resulting from a good compromise between morphology and structural characteristics.

Electrochemical stability is an important issue since anode electrocatalyst operate at high potentials. Chronopotentiometric tests at high current densities reveal that the anode electrocatalyst can be object of degradation when the potential exceeds 2 V (Fig. 7).

As above discussed, nanoparticles can be dispersed on Ti-suboxide or doped Ti/Sn-oxide supports in order to stabilise the active phase through a strong catalyst-support interaction



**Fig. 7** Stability characteristics at high current density for a PEM water electrolysis cell based on unsupported  $\text{IrO}_2$  anodes and Pt/C cathode electrocatalysts [6]

[20]. This could reduce electrochemical degradation e.g. dissolution and particle growth, which in most cases is promoted by the corrosion and agglomeration of unsupported catalysts. Preparation of catalysts for  $\text{O}_2$  evolution such as nanosized  $\text{IrO}_2$  particles highly dispersed on a high surface area (e.g.  $300 \text{ m}^2 \text{ g}^{-1}$ ) doped-oxide, or sub-oxide may thus allow a reduction of the present noble metal loading by one order of magnitude i.e. from 3 to  $0.3 \text{ mg cm}^{-2}$  while maintaining similar performances. A significant decrease of the overall cost for the device can mitigate the requirement to operate at economical but the same time extremely high current densities (e.g.  $2\text{--}3 \text{ A cm}^{-2}$ ) which are associated with high operating voltages causing a drastic decrease of the operating life as a consequence of the increased corrosion/degradation processes.

Regarding non noble metal formulations, several transition metal oxides with spinel structure or analogous perovskite-type formulations may be interesting for this application. Challenging aspects for these materials regard conductivity, electrocatalytic activity and stability. Proper enhancement of these relevant properties may be achieved by using an electrospinning procedure [20]. This method produces 1-D architectures [21] that may compensate the strong decrease of electronic percolation due to the absence of highly conducting precious metal oxide compounds. The high surface to volume ratio that characterise 1-D structures is also appropriate with regard to the high number of accessible catalytic sites for the OER [21].

### 3.2 Cathode electrocatalysts

Pt electrocatalysts are typically used as cathodes for the hydrogen evolution reaction in a PEMWE. Pt is required because it yields the best catalytic activity for the HER and also because of the strong acidity of the solid electrolyte, which would cause the corrosion of a non-noble metal. By comparing the electrochemical activity of several transition metals a volcano-shaped curve is obtained as a function of the strength of the metal-hydrogen bond formed [14].

Accordingly, for the metal with low bond strength, the adsorption of hydrogen is the rate-determining step, whereas for the metal with strong bond strength, the desorption of hydrogen is rate limiting. This means that metals with an intermediate bond strength, e.g. Pt, Ru, Rh, Re are the most active toward the HER. There is still a great interest to develop similarly active, selective and less expensive electrocatalysts for hydrogen evolution. As an example, Pd is three times less expensive than Pt and, if dispersed as nanosized particles on a carbon black support in the presence of catalytic enhancers, it may allow appropriate electrocatalytic activity to be achieved. This approach is actively pursued in the literature with regard to the tailoring of particle size (2–3 nm), the structural optimisation, the use of catalyst promoters and the development of core-shell structures with Pt on the surface and Pd forming the core of the particles [22]. This may be achieved by surface segregation of Pt.

As introduced above, at the present, highly dispersed carbon supported nanosized Pt particles are presently the benchmark electrocatalyst for polymer electrolyte membrane water electrolyzers. These materials are not much different than the conventional electrocatalysts used in fuel cells and thus they have been developed for several decades. At the moment, it appears that there is no much space to further improve conventional Pt/C catalysts. As already discussed, beside reducing Pt loading at the cathode, another promising research direction concerns with the use of a much cheaper Pd/C electrocatalyst, which is also less poisoned by water ion contamination. However, to enhance the electrocatalytic activity of Pd and to achieve performances comparable to Pt, at the same noble metal loading, the use of catalytic enhancers is necessary. Although quite promising from the catalytic point of view, catalytic enhancers often suffer from leaching phenomena under prolonged operation. The aim is to stabilize such systems and to create an appropriate chemical environment around Pd sites that may favour electro-adsorption of H-species.

Non-noble metal materials such as Ni that are in principle promising for  $\text{H}_2$  evolution are less stable in the PEMWE environment. However, their modification with a Ru overlayer may results in a suitable stability and electrocatalytic activity provided that Ru forms a skin layer over the Ni core. Dissolution of Ni atoms, that may be present on the catalyst surface, as Ni ions may irreversibly poison the polymer membrane.

### 3.3 Polymer electrolyte membrane

With regards to the separator material, the membrane generally used in PEM electrolysis is based on a perfluorosulphonic acid (PFSA) polymer such as Nafion<sup>®</sup> (e.g. N117 and N115). Nafion<sup>®</sup> is generally characterised by

high equivalent weight ( $1100 \text{ g eq.}^{-1}$ ) and the membranes commonly used in PEMWEs have a thickness of 120–170  $\mu\text{m}$ . The selection of the appropriate thickness results from a compromise between low area specific resistance, low cross-over and suitable mechanical stability requirements. The conductivity of Nafion<sup>®</sup> at 80 °C is about  $0.15 \text{ S cm}^{-1}$  and the associated area specific resistance of Nafion-117 is around  $0.15 \Omega \text{ cm}^2$ . Several alternative PFSA membranes with shorter pendant side-chain and higher conductivity have been developed by Dow, 3 M, Gore, Asahi glass and Solvay Specialty Polymers [23]. The polymers have shown an increased ionic conductivity with respect to Nafion in a wide range of operating conditions.

An important aspect of PEMWE operation is related to gas cross over. In the presence of cross-over, hydrogen and oxygen may react directly especially on the platinum sites at the cathode. This reaction is extremely exothermic, and produces a local heating that, with time, can destroy the membrane backbone structure or cause a strong catalyst sintering. Thus, low levels of  $\text{H}_2$  and  $\text{O}_2$  cross-over are necessary for PEMWE application due to the high pressure operation that may reach 50–100 bars. Thus, a proper thickness is necessary for the polymer electrolyte separator. For high pressure operation in PEM electrolyzers, reinforced PFSA membranes may provide a proper combination of good conductivity and high mechanical strength.

Concerning with high pressure operation of PEM electrolyzers, of relevant interest is the comparison of the mechanical properties of the different membranes. Besides the tensile properties, another mechanical property which is believed to be crucial in PEM electrolyser application is the tear resistance of the membrane. Actually, stresses can develop between the edge of the electrode and the gasket, causing catastrophic failure due to tearing of the membrane, with consequent hydrogen and oxidant mixing. Good thermal and visco-elastic properties as well as water absorption and mechanical behaviour including good tensile properties and low tear propagation resistance are the characteristics required for long term operation in PEM electrolyzers. Accordingly, regarding the development of new membranes, further progresses should concern mainly on the enhanced structural and mechanical robustness, which prevent the two gases from intermixing and the enhanced conductivity that reduces the electrolysis cell voltage allowing electrolytic hydrogen production at more competitive cost.

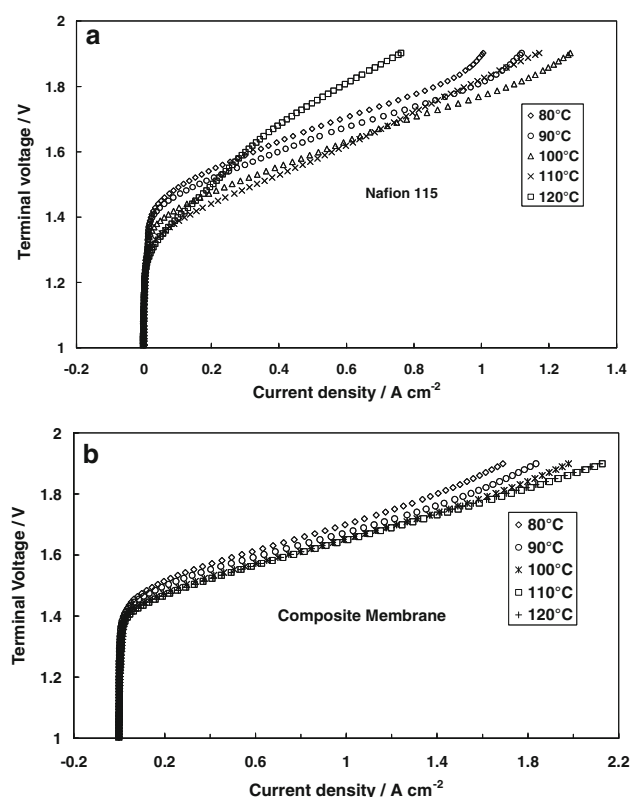
Besides the different conductivity and mechanical stability characteristics, further improvements concern with the development of proper ionomer dispersion for the catalyst-electrolyte interface. This can provide an increase of electrocatalyst utilisation.

Another approach aiming at reducing the cost incidence of electrolyte in PEMWEs is the use of cost-effective hydrocarbon membranes with suitable conductivity and better resistance than Nafion to cross-over. These membranes are non-perfluorinated electrolytes with interesting characteristics for electrochemical applications because of their low cost, wide commercial availability, and easy chemical processing [24, 25]. Proper interfacial properties and reduced cross-over characteristics, are also envisaged for composite organic–inorganic formulations, which make them very attractive for PEM electrolyzers operating under high pressure [24].

Electrolysis is an endothermic process; it needs a proper heat supply to operate at high temperatures. An increase of temperature causes a decrease of the Gibbs free energy change and an increase of the reaction kinetics. In general, operation of PEMWEs with photovoltaic or wind energy devices is appropriate at low temperatures (e.g. <100 °C). However, there are some cases where PEM electrolyzers can take advantage of the supply of waste heat. This may be the case of a thermal solar plant as renewable power source. Under such conditions, an increase of the operation temperature of the electrolyser should enhance the oxygen evolution reaction rate that is the rate-determining step of the entire process allowing to obtain high current and high conversion efficiency. The process may also take advantage of the more favourable thermodynamic conditions for water vapour splitting. However, the conductivity of Nafion membranes decreases at temperatures >100 °C due to membrane dehydration. Alternative membranes more suitable to high temperature operation, at least in the range of 120 °C with good mechanical properties and high Tg level would be appropriate. Composite membranes containing hygroscopic ceramic oxide fillers have been developed for high temperature fuel cells (up to 150 °C) [26–28]. The inorganic fillers enhance the water retention inside the composite membrane allowing the system to operate at high temperatures and, moreover, they decrease the cross-over by effect of the increased tortuosity factor induced by the presence of nanoparticles inside the membrane. Polarization curves in a wide temperature range for a PEM water electrolyser single cell based on a composite PFSA- $\text{SiO}_2$  membrane and Nafion 115 under pressurised operation are shown in Fig. 8. It is clearly observed that the composite membrane shows enhance performance in the high temperature operating range.

At high pressure, even above 100 °C, there is a good fraction of liquid water inside the system and the composite membranes should suffer much less from dehydration compared to Nafion. Moreover, the filler surface can be properly tailored to include recombination pathway promoters (Ce, Mn) that reduce the occurrence of hydrogen peroxide radicals generally caused by cross-over.





**Fig. 8** Polarization measurements for a PEM water electrolysis cell based on conventional Nafion 115 and composite PFSA-SiO<sub>2</sub> membrane at various temperature and 3.0 bar abs. pressure. Reprinted from Ref. [26] with permission from Elsevier

### 3.4 Membrane and electrode assembly

The next step to membrane and catalyst development is their validation in practical MEA structures and evaluation in a real electrolyser hardware under relevant test conditions especially for operation with renewable power sources. The MEAs play an important role in determining performance and stability for PEM electrolyzers. They contain backing layers, gas diffusion layers, catalytic layers and membrane. Significant research efforts are addressing the development of appropriate structures for the electrode as well as for the catalyst-electrolyte interface. This requires the investigation of a number of key factors such as composition, morphology, electrode thickness, pore volume, pore size distribution, hydrophilicity-hydrophobicity modulation and catalyst loading. As discussed above, proper ionomer development and incorporation in the catalytic layer allows a suitable extension of the triple-phase boundary with proper catalyst utilisation while maintaining appropriate structural integrity and diffusion path for water to reach the catalytic sites as well as escape of gaseous products.

The noble metal loading could be significantly reduced if catalyst utilisation is increased. Such enhancement could

be achieved if both anode and cathode electro-catalysts are tailored to be distributed on the outer surface of the support agglomerate in the case of supported catalysts; furthermore, an increase in dimension of support pores (mesoporous structure) and a decrease in the size of ionomer micelles are useful for increasing the contact region with the ionomer. One of the approaches is the direct deposition of the catalyst onto the membrane to form a catalyst coated membrane (CCM).

### 3.5 Stack hardware components

Generally Ti-based materials are used for backing layers (diffusion media) and bipolar plates current collectors. Often the anode backing layer is coated with a thin Pt overlayer to reduce contact resistance, mitigate passivation phenomena and at the same time it acts as a recombination catalyst. To decrease the cost of stack hardware, cheap alternative stainless steel components may be useful. However, these must be stable in acidic environment at the high operation potentials of PEMWE anodes. The non-active components of the stacks also need improvements in terms of materials selection to reduce degradation phenomena like passivation and release of metal ions [29].

A laboratory prototype of a short stack PEM electrolyser for low pressure operation and the related system is shown in Fig. 9. The PEM electrolysis system is quite compact and does not require significant maintenance efforts [30, 31]. For high pressure operation a round geometry for the stack design is preferred with respect to the squared geometry that may be more appropriate for low pressure.

The direct production of hydrogen at high pressure is an interesting improvement in the hydrogen storage problem because it allows reduction or even elimination of the compression of the hydrogen gas [32]. Electrolysers are often used coupled with multi-stage compressors to obtain the required final pressure, and H<sub>2</sub> compressors must be of particular construction, and have high investment costs. As an approach for electrolyser and process simplification, the high pressure can be maintained just in the cathode compartment; this may cause a pressure gradient across the electrolyte membrane. The main issues to deal with are the high mechanical stresses across the membrane, the need for low pressure drops in the water supply.

Appropriate stack hardware design and sealing concepts need to be developed for the specific operating conditions especially with regard to high pressure operation. Although an increase of pressure causes an increase of the thermodynamic potential for water splitting (about 100 mV increase at 10 MPa), the direct delivery of pressurised hydrogen to the storage tanks allows reduction of the energy consumption associated with gas compressors. However, there are several aspects that need to be



**Fig. 9** Laboratory prototype of a short stack PEM water electrolyser and PEM electrolysis system ( $\sim 0.3 \text{ Nm}^3 \text{ H}_2 \text{ h}^{-1}$ )

addressed i.e. the safety issues in accordance with the ATEX directive [33], the increase of gas permeation through the membrane (an increase of pressure causes a significant reduction of Faradaic efficiency through cross-over), the need for a thicker or reinforced membrane with higher specific resistance versus bare membranes of the same type, a lower gas purity and the need for recombination catalysts. The latter approach is necessary to favour a direct chemical recombination of the permeated gas over the surface of a highly dispersed catalytic bed to maintain the concentrations well below the hydrogen flammability limits in oxygen which are between 4.6 and 93.9 % [1, 2]

but preferably less than 1 %  $\text{H}_2$  in the  $\text{O}_2$  stream and, moreover, to improve hydrogen gas purity.

#### 4 PEM water electrolysis in combination with renewable power sources

PEMWEs were initially developed to provide oxygen for aerospace and submarines but the designs were readily adapted and upscaled to large hydrogen generation plants, even if not yet economically competitive. Small-scale systems are also commercialized for laboratory applications. Today PEMWEs are used to produce high purity hydrogen for fuel cells, hydrogen welding, metallurgy of pure metals and alloys, manufacture of pure substances for the electronics industry, analytical chemistry [34, 35]. Hydrogen can be directly burned inside an internal combustion engine or used in a fuel cell to power automobiles, as well as to provide electrical energy in rural areas or during peak demands (peak shaving). The PEMWE is more useful than the other technologies for operation with intermittent power sources. The electricity for the electrolyser can be supplied during off-peak times when extra electricity is available [1]. Wind and solar energy both in small and large-scale power plants are becoming a competitive choice with progressive reduction in investment cost and increasing price of fossil fuels.

As well known the main problem related with RES is due to their intermittent characteristics that can not be easily sustained by the actual grid. Although, special efforts are addressed worldwide to the development of smart grids, it should be considered that the best solutions are limited to local networks since the transport of electricity under long distances may result in specific losses [36]. The widespread diffusion of renewable sources implies that suitable storage solutions alternative to the grid must be considered. As frequently discussed, hydrogen can effectively play the role of an alternative energy storage and carrier. Although several processes have been developed for production of hydrogen from renewable energy sources, the most suitable one remains the water electrolysis. PEM electrolyzers can find suitable applications for peak shaving in integrated systems grid connected. All electric power supply companies provide electricity to the customers by using a period-related cost scheme. This takes into account the seasonal changes as well the specific power consumption during the day in order to increase the utilization of off-peak produced energy and reduce that of peak power [36]. This aspect is of relevant interest for energy saving. Similar aspects occur for grid independent operating conditions where hydrogen generated through electrolysis is stored and then via fuel cell converted back to electricity when needed or used to refill fuel cell based

cars. In this regard, hydrogen is the clean energy carrier to accomplish the sustainable production of energy and a synergy among hydrogen, electricity and renewable energy sources is achieved. The important economic advantage relies on the fact that the PEM electrolyser circumvents the problems related to the grid connection and generation of imbalance charges. In fact, the PEM electrolyser contributes to load leveling by changing operational current density in accordance with the change of electricity demand. It is operated under the higher current density during the off-peak period of electricity demand. On the other hand, it is operated under the lower current density during the daytime and peak period of electricity demand. Moreover start and stop cycles may be frequent in a PEM electrolyser and this represents a significant advantage with respect to a solid oxide-based water electrolyser and even if to a less extent with respect to alkaline electrolysers.

The electrolysis system can sustain much better than the grid a variable power supply and suitable power management strategies can be applied (power conditioning and control). For grid-connected systems, a suitable approach is to use electrolysers whose power consumption is a certain factor lower than the maximum power output of the renewable source. This due to the fact that the installed electrolyser capacity determines the economical sustainability of the entire system. Thus, it is really important to develop PEM electrolysers capable of operating for prolonged periods under variable conditions without suffering degradation for the active materials and hardware. This requires a relevant campaign of tests with different load profiles simulating a range of RES. Of course, it is preferable for such variable energy input to operate always the system under high efficiency conditions even if this sacrifices a little bit the performance and thus the economy of the investment [37]. In fact, in this case there are lower thermal management constraints with respect to operation in the very high current density range. The latter corresponds to a better utilization of the installed capital but to a lower conversion efficiency. On the other hand, there is a minimum for current density operation corresponding to a practical (economical) condition since an excessive reduction of current is also associated to a decrease of temperature that irremediably causes larger activation control for the process.

Grid independent operation is generally the preferred option if the renewable power source is allocated in remote area (as it often occurs). In this case, hydrogen can be transported through a pipeline over a long distance at lower costs than electricity transmission. There are however several aspects that need to be addressed for a grid-independent operation such as the size of electrolyser, the intermittent profile of the renewable energy source, output pressure and efficiency. For the latter, one of the

advantages of PEM electrolyser is a small variation of efficiency with size and the modularity which allow to tailor the water electrolysis process on the basis of the variable energy input. The decentralised hydrogen production may represent an important option for the future. This implies the use of small systems directly coupled to wind/solar sources for hydrogen generation and its storage at high pressure.

Renewable electricity supplies are currently being dedicated entirely to the electricity system to help reduce its present dependency upon fossil fuels. Yet, absorbing in Europe the planned inputs of intermittent renewable energy into the power system will become increasingly problematic. Once a large amount of renewable power has been integrated by 2020, the management of the power system will become difficult. To deal with this, electricity companies will need to integrate large amounts of energy storage and re-conversion systems while providing no added value for electricity consumers. In this context, storage in the form of hydrogen is particularly attractive, because it can be sold as a clean fuel at a premium price (especially in the transport sector where hydrocarbon fuels are already heavily taxed and there is a need of low/zero carbon fuels), or reconverted to electricity to satisfy demand at times when the renewable input is low. Thus, the generation of hydrogen by electrolysis may become a very important feature of the future power system; indeed it may become very important in permitting the continued expansion of intermittent renewable power sources.

## 5 Conclusions

R&D in innovative hydrogen production from renewable energy sources appears as a priority for the development of the future sustainable energy systems. Hydrogen technologies are in continuous development with a great number of applications and business sectors involved. Technologies for hydrogen utilization, such as fuel cells, can not be introduced and commercialised without proper technologies for hydrogen production and storage, and vice versa. Also hydrogen as energy vector without renewable energy makes much less sense.

In this work we have addressed the main issues concerning with the materials and development strategies of PEM water electrolysis. A proper analysis of the technology aspects can form a basis to assess the readiness for commercialisation and for future product development, having a long term perspective to meet the techno-economic challenges for hydrogen generation from PEMWEs as alternative to generation from fossil fuels. It appears that the existing hydrogen market provides a very large target for developers of low-cost electrolysers. However, the



potential of future hydrogen markets is much greater. Future applications for electrolyzers include supplying high volume markets in distributed applications (e.g. for refuelling fuel cell vehicles at all scales); buffering intermittent renewables technologies within electricity networks to facilitate power system management in a “high renewables” electricity sector; capturing intermittent renewable electricity supplies for dedicated hydrogen and oxygen production; and decarbonising large-scale industrial processes (e.g. ammonia production and furnaces). Several new markets may emerge for low/zero-carbon oxygen production including the use of electrolytic oxygen for oxygenation processes in the water industry, for oxygen-enrichment in furnaces, for oxy-hydrogen combustion processes and for very high-efficiency fuel cells. Thus, although the principal commercial purpose of an electrolyser will be to provide hydrogen, the value of the oxygen by-product should not be overlooked.

In general, it would seem the opportunities for achieving cheap electrolyzers will be limited by the increasing dominance of material costs, especially for PEM electrolyzers. However, the development of low-cost electrolyzers appears quite attractive, because the perspective hydrogen market is very large and the availability of alternative routes to producing hydrogen of zero/low carbon-footprint is limited.

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